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Recent advances in computational study and design of MOF catalysts for CO_2 conversion

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Catalytic conversion of the greenhouse gas CO_2 into value-added chemicals and fuels is highly beneficial to the environment, the economy, and the global energy supply. Metal–organic frameworks (MOFs) are promising catalysts for this purpose due to their uniquely high structural and chemical tunability. In the catalyst discovery process, computational chemistry has emerged as an essential tool as it can not only aid in the interpretation of experimental observations but also provide atomistic-level insights into the catalytic mechanism. This Mini Review summarizes recent computational studies on MOF-catalyzed CO_2 conversion through different types of reactions, discusses about the usage of various computational methods in those works, and provides a brief perspective of future works in this field.

KEYWORDS

computational chemistry, metal–organic framework (MOF), CO_2 conversion, density functional theory (DFT), computational catalysis

Introduction

Reducing the emissions of greenhouse gases, primarily CO_2, into the atmosphere to address climate change has become an urgent, global environmental issue in recent years. Numerous efforts have been made to develop efficient technologies for physically capturing CO_2 from the air *via* adsorption into solid-state materials or absorption into liquids (Yu et al., 2012). Going one step further, CO_2 can also be chemically converted into value-added chemicals and fuels, which not only reduces CO_2 emissions but also produces a useful feedstock for the chemical industry and boosts the global energy supply (Huang and Tan, 2014). However, CO_2 is highly stable and fairly inert, which makes such conversions energy intensive. If the energy cost would result in a net positive flow of CO_2, then the process is not accomplishing the task of reducing CO_2 emission. Developing efficient catalysts for CO_2 conversion under mild conditions is therefore necessary for making those reactions practically useful.

Recently, a large number of metal–organic framework (MOF) materials have been designed as CO_2 conversion catalysts and have shown promising performances (Beyzavi et al., 2015; Li et al., 2018; Li et al., 2020; Zhao et al., 2021a). MOFs are crystalline, nanoporous materials formed by the assembly of inorganic nodes and organic linkers in a

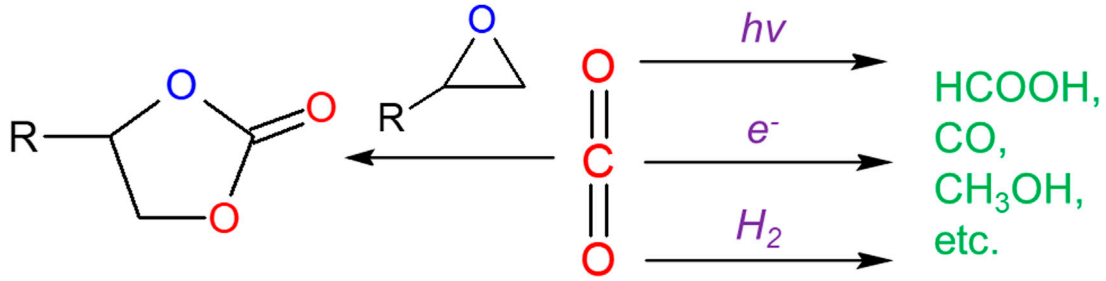

FIGURE 1
Main routes of CO_2 conversion into value-added chemicals and fuels.

TABLE 1 Comparison of cluster, periodic and multi-level models in computational catalysis.

Model	Pros	Cons
Cluster	• Small model size • More options on level of theory	• Truncation can be somewhat arbitrary • May omit key guest-pore interactions
Periodic	• Complete representation of system • Can start directly from crystal structure	• Large system (unit cell) size • Limited options on density functional
Multi-level	• Balance accuracy and cost	• Model construction is non-trivial

combinatorial fashion, which enables fine-tuning of their structural and chemical properties *via* atomically precise design. The excellent structural integrity of MOFs also greatly facilitates computational studies, which often require well-defined atomic coordinates as starting points. Due to the rapid development in methods, algorithms and computing power, computational chemistry has become an essential tool in the investigation of a wide variety of chemical problems. Computational studies not only complement experiments by delivering atomistic-level explanation on experimental observations but also possess increasing predictive power in searching for molecules/materials with even better performance in a certain application. Indeed, many synergistic computational-experimental studies on MOFs for catalytic CO_2 conversion have been published in recent years, which will be discussed in the following sections of this Mini Review.

Catalytic conversion of CO_2 into cyclic carbonates

The most studied route of catalytic CO_2 conversion into value-added chemicals is the cycloaddition between CO_2 and epoxides (Figure 1), which produces five-membered cyclic carbonates (CCs). CCs are versatile chemicals which can be utilized as solvents, battery electrolytes and building blocks in the synthesis of plastics and pharmaceuticals. Schaffner et al. (2010) This reaction also has a remarkable atom economy of 100%. Since the first report of MOF-catalyzed cycloaddition between CO_2 and epoxides in 2009 (Song et al., 2009), a wide variety of MOFs have been tested for this reaction, in which the catalytic mechanism could vary significantly among different MOFs.

Cluster-based density functional theory (DFT) calculations have been routinely employed to carve out the active site cluster from the periodic MOF structure, map out the reaction pathways and calculate the energy barriers to elucidate the catalytic mechanism (Table 1; Figure 2). Beyzavi et al. (2014) discovered that the MOF Hf-NU-1000 can catalyze the epoxide ring-opening step of this reaction by donating protons from the ligated aqua and OH ligands on its Hf-node. For aromatic substrates, the aromatic rings in the linker can further stabilize the transition state (TS) *via* π-stacking. Kathalikkattil et al. (2015) synthesized and studied an eco-friendly Zn-glutamate MOF which catalyzes CO_2-propylene oxide (PO) cycloaddition through synergistic involvement of Lewis acid (Zn), Lewis base (amino groups in glutamate) and ring-opening nucleophile (bromide anion from the co-catalyst tetrabutylammonium bromide (TBAB)). Hu et al. (2018) studied the same reaction catalyzed by the Cr-MIL-101 MOF in the presence of TBAB and certified the importance of the synergistic catalytic effect between Lewis acid (Cr) and nucleophile (TBAB). The co-catalyzed reaction was found to have a much lower barrier (18 kcal/mol) than the Cr-MIL-101-alone catalyzed

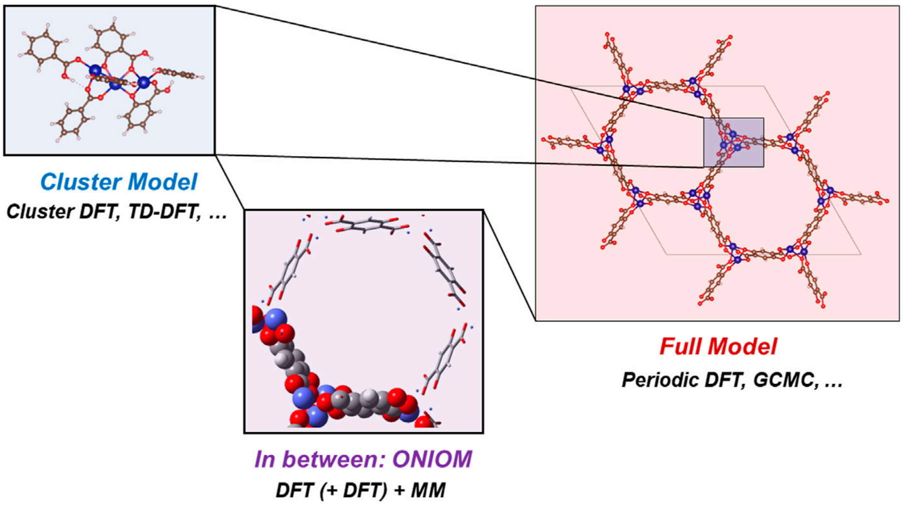

FIGURE 2
Illustration of different levels of models in computational study of MOFs.

(47 kcal/mol) and the TBAB-alone catalyzed (27 kcal/mol) reactions. Similar synergistic effects were observed by Rachuri et al. (2019) and Wang et al. (2021) in a Zn/Cd-adenine MOF and in a Cu_{12} nanocage-based MOF, respectively. Parmar et al. (2019) showed that iodide can act similarly as bromide in the ring-opening step and mapped out the reaction pathway of CO_2 cycloaddition onto an epoxide-bearing oxindole catalyzed by a Co-MOF and potassium iodide. Ma et al. (2022) designed a Cd-MOF with dynamic metal-iodide bonds that can release iodide anions to facilitate the ring-opening step, which was then confirmed by DFT calculations. Yang and Jiang. (2022) combined DFT calculations and wavefunction analysis to elucidate that the regioselectivity in CO_2-PO cycloaddition co-catalyzed by Cu-MFU-4l/TBAB is a result of the competition between electronic and steric effects.

Without a bromide or iodide cocatalyst, efficient CO_2 conversion to CC has also been achieved with MOF catalysts. Wu et al. (2019a), Wu et al. (2019b) designed a series of MOFs with format linkers and nitrogen-containing ligands which showed good catalytic performance. DFT calculations helped elucidate the role of those ligands in the reaction, which is to activate CO_2 by increasing the nucleophilicity of its oxygen atom for easier nucleophilic attack on epoxide. Dhankhar et al. (2021) also observed in a Cu-MOF with nitrogen-rich linkers that the nitrogen-containing functional groups on the linker can activate CO_2 to facilitate nucleophilic attack, with the help of DFT calculations.

In the aforementioned ten computational works, four density functionals have been used: M06 (Zhao and Truhlar, 2008), M06-2X (Zhao and Truhlar, 2008), M06-L (Zhao and Truhlar, 2006), and B3LYP. Vosko et al. (1980), Lee et al. (1988), Becke. (1993) M06, M06-2X, and B3LYP are among the most widely used functionals in computational chemistry due to their versatility and robustness, while M06-L has been extensively used for transition metals. Besides cluster-based DFT, periodic DFT has also been employed to investigate this catalytic reaction, which eliminates the procedure of carving out the active site cluster by including the entire periodic structure in the calculation (Table 1; Figure 2). However, due to the high computational cost associated with large unit cells of MOFs (often hundreds of atoms) and limited options on functionals (using hybrid functionals such as B3LYP often increase the computational cost significantly in periodic systems), the usage of periodic DFT in MOF catalysis is less common (albeit on the rise recently). The only reported mechanistic pathway mapped out by periodic DFT in MOF-catalyzed CO_2-to-CC conversion to date is by Luo et al. (2019), who used the PBE (Perdew et al., 1996) functional with plane-wave basis sets to study this reaction catalyzed by a Zn-MOF.

To get the benefits of both cluster and periodic DFT, multi-level methods such as ONIOM (Chung et al., 2015) has been adopted (Figure 2). In ONIOM, the system is divided into multiple layers, each of which can be described using a different level of theory to balance accuracy and cost (Table 1). Xu et al. (2018a) constructed a two-layer ONIOM model to study the cycloaddition between CO_2 and styrene oxide catalyzed by Co/Mg-MOF-74, in which an inner layer of 105 atoms around the active site were described using B3LYP while the rest of the system as an outer layer was described by molecular mechanics (MM). Li et al. (2019) adopted a similar strategy to study the cycloaddition between CO_2 and propylene oxide catalyzed by a Cu-MOF NTU-180 and TBAB, in which M06-L was selected for the inner layer. Compared with cluster-based DFT, ONIOM can better capture the noncovalent interactions that the substrates “feel” in the MOF pores, which may be crucial in certain cases.

Besides mapping out mechanistic pathways, computational methods can help better understand this catalytic reaction in other ways. Zhang et al. (2016), Sharma et al. (2018) and Kong et al. (2021) carried out DFT calculations to locate the most favorable binding sites of CO_2 in different MOFs as starting points of mechanistic investigations. Parmar et al. (2019) performed grand canonical Monte Carlo (GCMC) simulations with MM force fields to obtain the sorption isotherm and binding sites of CO_2 in their Co-MOF, prior to DFT study on cycloaddition reaction pathway. Liao et al. (2020) combined GCMC and DFT to get both the spatial distribution and binding energy of CO_2 in a Cu-MOF named HNUST-9, which exhibited high catalytic activity in CO_2-to-CC conversion. Müller et al. (2019) performed GCMC simulations to screen 12 computationally-generated MOF structures made of the same linker but different inorganic nodes and topologies for CO_2 adsorption. The one with highest CO_2 uptake was then synthesized and exhibited high catalytic activity in CC production.

Photocatalytic reduction of CO_2 into fuels

Another important category of CO_2 conversion reactions is the reduction of CO_2 into fuels such as HCOOH, CO, CH_3OH and CH_4 (Figure 1), also known as “artificial photosynthesis.” This process allows carbon to be reused and can help achieve a carbon neutral economy. Due to the high thermodynamic stability of CO_2, photochemistry is often used to facilitate its reduction. Dhakshinamoorthy et al. (2016) These reactions involve complicated processes such as excitation/emission and electron transfer, which makes computational mechanistic investigations even more useful.

MOFs with photosensitive structural units such as porphyrin/Ru $(bpy)_3$ (and analogs) in the organic linkers and redox-active metals in the inorganic nodes can be used as photocatalysts. For example, Wang et al. (2019a) performed a thorough computational study on CO_2 photoreduction catalyzed by Co-porphyrin (CoP) and a series of 2D CoP-based MOFs (Co/Zn/Zr-CoPMOF) using periodic DFT calculations. The electronic properties of the MOFs were studied by calculating the partial density of states (PDOS), which confirmed that the *3d* states of Co in CoP contribute dominantly to the valence bands (VB) near Fermi level in all those MOFs. Interestingly, the *3d* states of Co in Co-oxo clusters in Co-CoPMOF also has significant contribution to the same VB region and formed a low-energy conduction band (CB), which was not observed in Zn/Zr-CoPMOF or CoP itself. This results in a much narrower band gap of Co-CoPMOF (1.2 eV) compared to others (1.6–1.7 eV) and a higher light absorption ratio in Co-CoPMOF (confirmed by absorption spectra calculations), which could lead to easier electron transfer and higher photocatalytic activity. Indeed, subsequent DFT calculations showed that the CO_2 to CH_4 photoreduction followed the same reaction pathway on all those catalysts and had the same rate-determining step, but Co-CoPMOF had the lowest energy barrier among them. Jin. (2020) conducted a combined experimental-computational study on CO_2-to-formate photoreduction catalyzed by three Zr-MOFs (PCN-222/223/224) with Zn-porphyrin linkers and showed that the catalytic activity may be correlated with the CO_2 binding energy on Zn-porphyrin. Yan et al. (2018) discovered high catalytic activity of CO_2 to formate photoreduction in the Eu-Ru $(phen)_3$-MOF and showed by DFT that a water molecule coordinated to Eu can be replaced by CO_2 (possibly assisted by light irradiation) to facilitate following reactions. Elcheikh Mahmoud et al. (2019) utilized time-dependent DFT (TD-DFT) to calculate the absorption spectra of a Ru $(cptpy)_2$-based Zr-MOF AUBM-4 and showed that its photocatalytic activity in CO_2 reduction should come from the Ru-to-cptpy metal-to-ligand charge transfer (MLCT) rather than the Ru-to-Zr metal-to-metal charge transfer (MMCT). Gao et al. (2020) and Stanley et al. (2021) incorporated Ru $(bpy)_3$ and its analogs into UiO-67 and MIL-101-NH_2, respectively, for photocatalytic CO_2 reduction and conducted DFT calculations to study the reaction mechanism. Sun et al. (2015) doped Ti into the Zr-node in UiO-66-NH_2 and observed enhanced photocatalytic activity in CO_2 reduction. DFT calculations and PDOS analysis revealed that the addition of Ti creates a low-energy CB and facilitates charge transfer. The reduced Ti (Ti^{3+}) can further reduce Zr^{4+} to Zr^{3+} through MMCT which is catalytically active, therefore acting as a mediator in the charge transfer chain. Wang et al. (2018a), Han et al. (2018), and Wang et al. (2019b) used DFT calculations to show the importance of CO_2-metal binding energy on the photocatalytic activity in Co/Ni-based MOFs and provided strategies to tune this binding energy *via* structural modification.

MOFs have been integrated with other materials to form composite photocatalysts for CO_2 reduction, in which computational methods have also been employed for mechanistic investigation. Xu et al. (2018b) integrated BIF-20, a Zn-MOF with high density of exposed B-H bonds, with graphitic carbon nitride (g-C_3N_4) nanosheets. DFT calculations and electron density analysis demonstrated that upon receiving photoexcited electrons from g-C_3N_4, B-H groups can trap the electron and strengthen CO_2 binding for subsequent reduction reaction. Jiang et al. (2020) grew photosensitive TiO_2 clusters inside the pores of MIL-101 and conducted periodic DFT calculations to find out possible electron transfer pathways. Benseghir et al. (2020) used DFT calculations to obtain the spatial distribution of polyoxometalate (POM) clusters in UiO-67 and elucidated the origin of enhanced photocatalytic activity of this MOF-POM composite. Olowoyo et al. (2020) utilized a semi-empirical tight-binding method to determine the orbitals in Ti-based MIL-125-NH_2 to understand its photocatalytic activity in CO_2 reduction. Yu et al., (2021) used DFT to elucidate the catalytic mechanism of CO_2 reduction in UiO-66-MoS_2 composite, in which the bridging Mo-O-Zr motif facilitates charge transfer from MoS_2 to Zr^{4+} to generate catalytically active Zr^{3+}.

Catalytic electro reduction of CO_2 into fuels

Electro catalysis is another solution to facilitate difficult redox reactions such as CO_2 reduction (Figure 1). MOFs, despite having the aforementioned advantages as catalysts, have not been extensively used as electro catalysts until recently due to their often poor conductivity. Downes and Marinescu. (2017) With the discovery of more conductive MOFs as well as MOF-based composites, computational methods have been employed to study the mechanism of catalytic electroreduction of CO_2.

Wang et al. (2018b) designed a POM-metalloporphyrin MOF in which the electron-rich low-valent metals (Mo(V)) in POMs and the macrocycle conjugated π-electron system in metalloporphyrin can boost the electrocatalytic activity together. Periodic DFT calculations showed that the energy barrier of CO_2-to-CO reduction in this MOF is much lower than in POM or metalloporphyrin alone, supporting the hypothesis of synergistic involvement of POM and metalloporphyrin in electron mobility. Huang et al. (2020) used DFT calculations to show that coordinated halogen anions on the Cd metal sites in Cd-metalloporphyrin MOFs NNU-17/18 can help activate bound CO2 molecules for subsequent electroreduction. Zhong et al. (2020) developed 2D Cu-Zn bimetallic MOFs for CO_2-to-CO electroreduction and revealed different roles of Cu and Zn centers in the catalysis using periodic DFT. Zhu et al. (2021) discovered from DFT calculations that a non-traditional C–H···O hydrogen bond played an important role in stabilizing the adsorbed *CHO intermediate during CO_2 electroreduction catalyzed by the MOF Cu-MFU-4l. Majidi et al. (2021) observed high activity towards CO_2 electroreduction at low overpotentials in a conductive 2D Cu-tetrahydroxyquinone MOF and used periodic DFT to map out the free energy profile. Zhao et al. (2021b) and Kang et al. (2020) combined Cu-based MOFs with Cu nanoparticles and Cu-foam electrodes, respectively, for CO_2 electroreduction and conducted DFT calculations to map out the reaction pathways.

Catalytic chemical hydrogenation of CO_2

Despite many challenges, pure chemical (without photo/electro catalysis) reduction of CO_2 in MOFs has still been made possible, which is mostly achieved by using H_2 as the reductant to form HCOOH (Figure 1). This requires the heterolytic dissociation of H_2 to a proton and a hydride, which can then attack the oxygen and carbon on CO_2, respectively. Frustrated Lewis pairs (FLPs), in which active Lewis acid and Lewis base groups are separated by steric hinderance, can both bind CO_2 (Ashley and O'Hare, 2013) and heterolytically dissociate H_2 (Stephan and Erker, 2010). The porosity and tunability of MOFs make them excellent platforms for incorporating FLPs. Ye and Johnson (Ye and Johnson, 2015a; Ye and Johnson, 2015b; Ye and Johnson, 2016; Ye et al., 2018) have conducted a series of computational work on exploring MOF-based FLPs for CO_2 hydrogenation. They first studied (Ye and Johnson, 2015a) the mechanism of CO_2 hydrogenation catalyzed by boryl-pyrazole-based FLPs incorporated in UiO-66 using periodic DFT, in which they obtained a low energy barrier but also found that H_2 needs to interact with FLP before CO_2. Otherwise, the barrier increases significantly due to the strong CO_2-FLP binding. They then conducted (Ye and Johnson, 2015b) a computational screening by varying the functional groups on FLP and observed a nearly linear correlation between H_2 binding energy and CO_2 hydrogenation barrier—stronger H_2 binding leads to higher CO_2 hydrogenation barrier. A Sabatier analysis was then carried out to determine the FLP with optimal trade-off between those two quantities. They also extended the scope of their work by studying further hydrogenation to CH_3OH (Ye and Johnson, 2016) and exploring other MOFs (Ye et al., 2018). In the latter work (Ye et al., 2018), GCMC simulations were also performed to identify MOFs with high CO_2 adsorption capacity. Yang and Jiang. (2020) created a FLP in UiO-66 by simply removing one bidentate carboxylate linker from the node and putting a hydroxide ligand on one of the two newly-created open Zr sites to balance the charge. DFT calculations confirmed that the other open Zr site and the hydroxide can act as (frustrated) Lewis acid and base, respectively, to catalyze CO_2 hydrogenation. Heshmat. (2020) revisited the reaction investigated by Ye and Johnson (2015a) using periodic DFT-based *ab initio* molecular dynamics (AIMD) simulations with meta dynamics for enhanced sampling. A stepwise pathway was found to be more favorable in AIMD in contrast to the concerted pathway observed from static DFT, suggesting more mechanistic possibilities for these reactions.

Chemical hydrogenation of CO_2 without FLP has also been achieved using other MOF-based catalysts, most with open metal sites. Maihom et al. (2013) conducted DFT calculations to show that Cu-alkoxide-functionalized MOF-5 can largely reduce the barrier in CO_2-to-HCOOH hydrogenation. An et al. (2019) and Zhang et al. (2021) incorporated Cu/Zn on the nodes in Zr-MOFs and observed synergistic catalytic effect between Cu/Zn and Zr in CO_2 hydrogenation. Qi et al. (2021) combined experiments and DFT calculations to show that in metalloporphyrin-based PCN-224, the Zr-node and the Cu-porphyrin catalyzed different segments of the CO_2-to-ethanol reaction. Krishnan et al. (2022) computationally screened metalloporphyrin-based MOF-525 (similar to PCN-224) with different metal centers for CO_2-to-HCOOH hydrogenation and identified Rh and Ir as best candidates. Yang and Jiang. (2021) computationally explored MOF-supported N-heterocyclic carbene-stabilized metal hydrides for catalytic CO_2 hydrogenation to produce methanol. Gutterod et al. (2020a), Gutterod et al. (2020b), Zhu et al. (2020) and Mori et al. (2020) incorporated Pt/Cu/PdAg nanoparticles in MOFs for CO_2 hydrogenation and conducted synergistic experimental-computational works to study the nanoparticle-MOF interactions and the catalytic mechanism.

Conclusion and perspectives

In conclusion, computational chemistry has emerged as an essential tool in the study and design of MOF-based catalysts for CO_2 conversion, particularly for providing atomistic-level insights and mapping out mechanistic pictures. DFT-based structural optimizations, energy calculations, transition state searches and wavefunction analyses have been routinely employed in the workflow. With the rapid development of new theoretical and computational methods, we believe that more state-of-the-art tools beyond regular DFT calculations will be applied to this problem in the near future, including but not limited to advanced wavefunction theory-based methods, machine learning (ML)-based potentials and AIMD. Nevertheless, rigorous testing and comprehensive benchmark calculations should be carried out to establish more robust and transferrable computational protocols. Moreover, with the recent development of robust high-throughput DFT/ML workflows for MOFs (Rosen et al., 2019; Rosen et al., 2021; Rosen et al., 2022a; Rosen et al., 2022b) and the establishment of large MOF structure databases (Wilmer et al., 2011; Chung et al., 2014; Colón et al., 2017; Moghadam et al., 2017; Chung et al., 2019; Li et al., 2021; Rosen et al., 2021; Rosen et al., 2022b), high-throughput computational screening can be adopted to exponentially accelerate the discovery of new MOF catalysts for CO_2 conversion. We believe that computational chemistry study will become an integral part in the massively collaborative effort to solve the omnipresent global climate crisis *via* carbon capture and utilization.

Author contributions

HC contributed to the conceptualization, literature survey, and manuscript writing.

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Conflict of interest

The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

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